

Printing Gold Nanoparticles with an Electrohydrodynamic Direct-Write Device

S.R. Samarasinghe^{*}, Isabel Pastoriza-Santos[§], M.J. Edirisinghe^{*=}, M.J. Reece⁰ and Luis M. Liz-Marzán[§]

^{*}Department of Mechanical Engineering, University College of London, Torrington Place, London, WC1E 7JE, UK

⁰Department of Materials, Queen Mary, University of London, Mile End Road, London, E1 4NS, UK

[§]Department of Physical Chemistry, University of Vigo, Vigo 36310, Spain

Abstract

A dispersion containing 15nm gold particles in ethanol was subjected to electrohydrodynamic atomization, producing droplets with an average size of $\sim 26\mu\text{m}$ as measured by laser diffraction. An electrohydrodynamic direct-write device was used to deposit the dispersion onto silicon wafers with the intention of printing gold tracks. Immediately after deposition ethanol evaporated, leaving the gold particles organised in a $\sim 75\mu\text{m}$ wide central region surrounded by two regions, each $\sim 50\mu\text{m}$ wide, at the edge of which two further gold tracks, each $\sim 7\mu\text{m}$ existed.

Keywords

nanoparticles, nano-suspensions, printing, direct writing, patterning, electrohydrodynamic, atomization

Introduction

Gold and gold alloys are important functional materials (1-3). Gold has been a mainstay in the semiconductor and electronics industry with applications such as high temperature monitoring circuits in aerospace, automotive applications (2) and microwave electronic fabrication (3). However, as the demand for electronic, photonic and bio-electronics technology rapidly increases, the utilization of gold and its alloys will be thoroughly scrutinized, particularly in terms of cost and efficiency. Current gold track depositing techniques are ink-jet printing, electron-beam or laser driven and tend to use organometallic precursors (2, 4, 5). The cost, yield and purity of such routes are of concern and motivated us to use a gold colloid to direct-write gold tracks in a more economical way.

Direct write using ink-jet printing is known as the prime technique for depositing and patterning functional materials in the liquid phase onto a substrate (6). Modified ink-jet methods such as laser cured ink-jet technology (7) can generate microdroplets in the range of $60 - 100\mu\text{m}$. However, as demonstrated in the traditional piezo-head technology based ink-jet printing of a gold track (8), it is well known that in ink-jet printing the droplets generated are larger than the nozzle's diameter and even if a fine ($65\mu\text{m}$ diameter) ink-jet nozzle is used, the deposited droplet relics are well over a $100\mu\text{m}$ in diameter. In contrast, the electrohydrodynamic process allows much coarser nozzles ($200-500\mu\text{m}$ in internal diameter) to be used, yet droplet and deposited droplet relics of less than $50\mu\text{m}$ can be achieved (9,10).

The electrohydrodynamic process usually consists of two electrodes, the first being a nozzle (needle) below which a second electrode (usually grounded) is held. The second electrode can be a ring, a plate or a point. An electric field is applied between the needle and the ground electrode while a suspension flows at a controlled rate through the needle. The surface of the flowing medium is subjected to an electrical stress and deforms locally to form an elongated jet, which subsequently evicts from the body of liquid, basically when the electric field is high enough to overcome the surface tension. The jet disintegrates into droplets. The geometry of jetting is classified into different modes of spraying (11,12) and it is well known that the stable cone-jet mode makes it possible to regularise the break-up of the jet to generate droplets of tens of micrometers in size, which are also highly uniform in size. A ring or plate shaped second electrode allows the droplets to diversify and is useful in the preparation of nano-sized and other powders (13,14) and coatings and films (15,16) but, in contrast the use of a pointed second electrode helps to focus the droplets and direct write (17). Furthermore using a lower flow rate and higher applied voltage produces smaller droplets (18) and this helps to minimize the size of printed lines.

In this paper, we report our initial findings on the electrohydrodynamic deposition of a very dilute gold alcosol

⁼ Corresponding author: m.edirisinghe@ucl.ac.uk

and the resulting track formation. A more extensive study on different alcosols and the assessment of track properties achieved is underway.

Experimental

Preparation of gold alcosol

Tetrachloroauric acid ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) and trisodium citrate were purchased from Aldrich. Poly(vinylpyrrolidone) (PVP, MW 10,000) was supplied by Fluka. All chemicals were used as received. Milli-Q water was used to make up all solutions ($R > 18.2 \Omega \text{ mm}$).

Gold nanoparticles with an average diameter of around 15 nm and 10% polydispersity were synthesized according to the standard sodium citrate reduction method (19) by boiling $5 \times 10^{-4} \text{ M}$ HAuCl_4 in the presence of $1.6 \times 10^{-3} \text{ M}$ sodium citrate for 15 min. After cooling down, the particles were transferred into ethanol upon functionalization with PVP (20). Briefly, an amount of PVP sufficient to coat the particles with 60 PVP monomers per nm^2 surface was dissolved by ultrasonication for 15 min in water and added to the gold colloid. The polymer was allowed to adsorb to the gold particles overnight while stirring. The particles were subsequently centrifuged (3500 r.p.m.) to remove the unbound PVP and redispersed in ethanol which was used as the liquid carrier as with our previous work on electrohydrodynamic materials processing. The final gold colloidal dispersion contained 0.1 wt % gold particles.

Electrohydrodynamic studies

The equipment used (Figure 1a) consisted of a stainless steel needle with internal and external orifice diameters of $\sim 200 \mu\text{m}$ and $\sim 400 \mu\text{m}$, respectively, and held in epoxy resin. The needle was connected to a high voltage power supply (Glassman Europe Ltd., Tadley, UK) and the applied voltage was raised gradually to 5kV with respect to the ground electrode, which was a pointed rod. The inlet of the needle was connected to a Harvard PHD 4400 programmable syringe pump (HARVARD Apparatus Ltd., Edenbridge, UK) using a silicone rubber tube, and the flow rate of suspension to the needle exit was varied between $10^{-10} - 10^{-11} \text{ m}^3\text{s}^{-1}$. A fibre optic light source was used for illumination. A microscope lens in conjunction with a high speed camera (Weinberger AG, Dietikon, Switzerland), which was connected to a portable computer, allowed observation of the colloid while undergoing atomization.

Droplet sizing

The droplet size distributions resulting from the atomization of the alcosol were measured using a model KF Sympatec helium laser optical spectrometer sizing system (Sympatec

Ltd., System Partikel-Technik, Bury, UK) in conjunction with a computer for recording and plotting of data as in our previous work (21,22). The laser system was incorporated in the electrohydrodynamic atomization equipment by placing it so that the 2.2mm diameter laser beam was approximately just below the exit of the needle in order to try and simulate the direct writing experimental conditions given below (Figure 1b).

Direct writing

The device used consists of a stepper motor driven 2D system. The X and Y tables are mounted on one another keeping the 2-axis profile very low and the system is computer-controlled using a programmable motion controller. A datum and an end of travel limit sensor are fitted on each of the tables to trigger the controller when a respective carriage reaches a limit. A Perspex table is mounted firmly on the 2-axis system. The top of the table accommodates a frame for holding firmly up to an A4 sheet

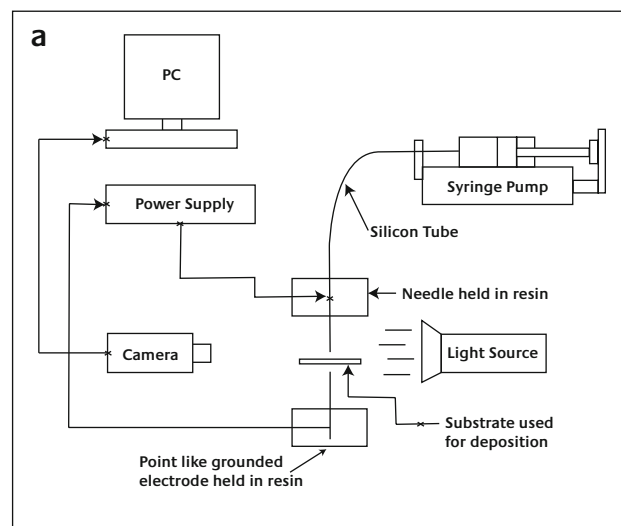


Figure 1
Equipment set-up used in: (a) electrohydrodynamic experiments
(b) droplet size measurement

of substrate. Using motion planner software X and Y coordinates can be created and downloaded to the 2-axis controller, allowing the 2-axis system to write the path described by the coordinates provided.

After the 2-axis system was set-up, the needle and point were aligned. Subsequently, the substrate, a silicon wafer, was placed $\sim 0.4\text{mm}$ below the needle. The silicon wafer used was boron doped P-type, $525\mu\text{m}$ thick and having a 400nm SiO_2 layer on both sides. Throughout writing the grounded point electrode was kept at a distance of $\sim 4\text{mm}$ below the substrate. A potential difference was applied between the needle and the point while the suspension was pumped through the needle at a pre-determined flow rate. The equipment used in this part of the process was identical to those used in electrohydrodynamic experiments described above.

The printed tracks were dried for 24 hours at room temperature and coated with carbon before examination by scanning electron microscopy and energy dispersive X-ray analysis. The SEM characterization was carried out with a JEOL JSM-6700F FEG-SEM operating at an acceleration voltage of 15 kV in lower secondary electron image (LEI) and at 10 kV in backscattering electron image (YAG). The elemental analysis was performed with an Oxford INCA Energy 300 X-ray Energy Dispersive Spectrometer (EDS) system.

Results and discussion

The alcosol is very stable and no sedimentation occurred on standing for several days. For classical electrohydrodynamic atomization (EHDA) to occur, the hydrodynamic time (t_h) must exceed the electrical relaxation time (t_e), and the inequality $\frac{LD^2}{Q} \gg \frac{\beta\epsilon_0}{K}$ must be satisfied (23).

L denotes the axial length of the jet, D is the jet diameter, Q is the flow rate, K is the electrical conductivity and β is the relative permittivity. ϵ_0 is the permittivity constant and is $8.85 \times 10^{-12} \text{ Fm}^{-1}$.

In our electrohydrodynamic experiments, the flow rate (Q) and applied voltage were kept constant at $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and 4.8 kV, respectively, as these conditions generated a stable cone-jet (Figure 2), which is well known to produce a monodisperse stream of fine droplets. D and L measured were $\sim 15\mu\text{m}$ and $\sim 325\mu\text{m}$, respectively, giving an electrohydrodynamic time of $1.46 \times 10^{-3} \text{ s}$. Using the β and K values of ethanol as 26 and $3.4 \times 10^{-4} \text{ Sm}^{-1}$, respectively (24) t_e is $6.77 \times 10^{-7} \text{ s}$. Thus $t_h \gg t_e$ and the condition required for classical EHDA is satisfied. The 0.1 wt. % of gold can only make the K value even higher to satisfy this inequality even more comfortably, but a high K value can impose an upper limit on the flow rate (25).

High applied voltages and lower flow rates are beneficial to print finer tracks as explained earlier. However, in general, increase of applied voltage resulted in discharge and at lower flow rates a stable cone-jet could not be maintained. Also the

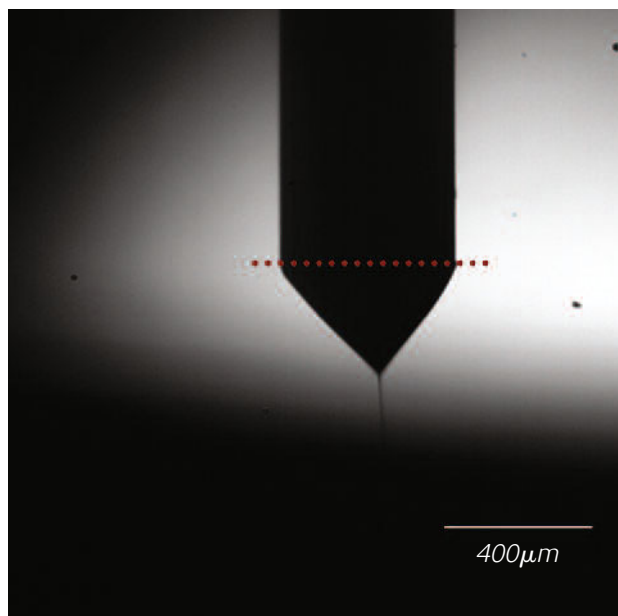


Figure 2

Stable cone-jet mode of electrohydrodynamic atomization of the gold alcosol at 4.8kV and $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$. Exit of the needle is indicated with a dotted line

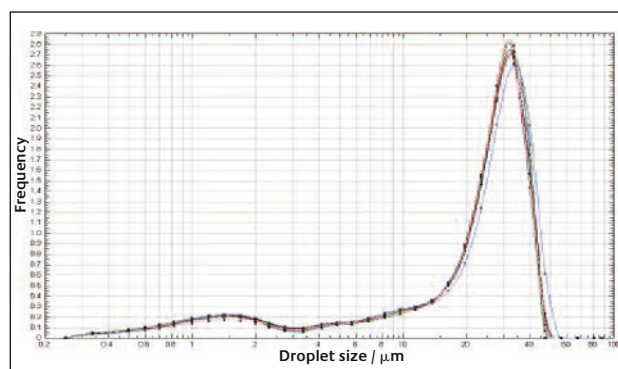


Figure 3

Typical droplet size distribution obtained by electrohydrodynamic atomization of the gold alcosol. Duplicate plots refer to repeated experiments

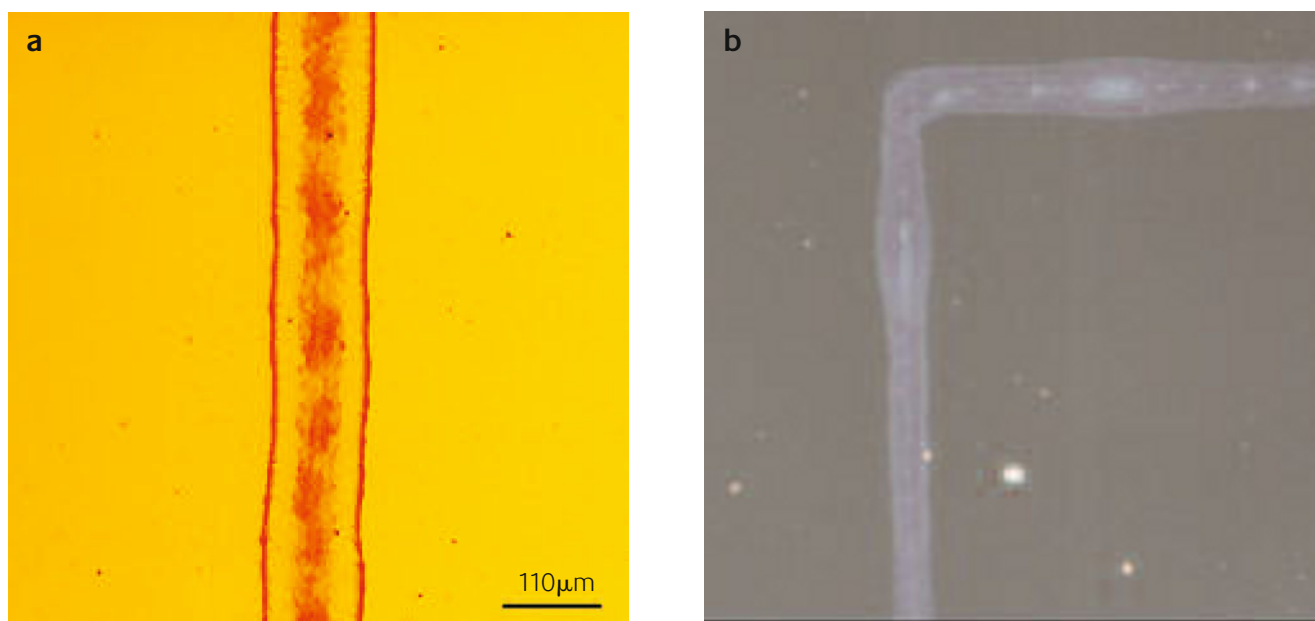
distance between the needle and the substrate was selected as 0.4mm and the distance between the substrate and the ground electrode was set at 4mm because they gave the finest line width without scattering of the droplet relics. When the distance between the substrate and needle, substrate and ground electrode was increased it produced a significant amount of scattering and when the distance was decreased, a stable cone-jet was not achieved.

The droplets generated by the cone-jet was in the range of $0.25\mu\text{m}$ - $60\mu\text{m}$ (Figure 3). The average droplet size was $\sim 26\mu\text{m}$ and the standard deviation was $5.7\mu\text{m}$. Different track geometries were prepared (Figures 4a and b) and the finest gold track deposited was $\sim 110\mu\text{m}$ wide. However, immediately after deposition, the gold nano-particles organised into narrow sub-tracks (Figure 5a). The typical width of the middle track was $\sim 75\mu\text{m}$ and the tracks at the boundary were $\sim 7\mu\text{m}$. Energy dispersive x-ray analysis confirmed that these regions of the original printed tracks

Table 1

A summary of results from investigations attempting the forming of conductive tracks. Parenthesis indicates the references

| Method | Solution | Particle size | Metal (wt. %) | Minimum Track Size |
|--|---|---------------|---------------|--------------------|
| Chemical e-Beam Lithography (27) | Citrate-passivated gold nanoparticles | 16nm | - | 100nm |
| Fountain Pen (28) | Gold nanoparticles in toluene | 2-4nm | 30 | 5 μ m |
| Micro-contact electroless plating technique (29) | Gold nanoparticles in colloid solution | 3nm | - | 5 μ m |
| Laser direct write (30) | Gold Ink | - | - | 8 μ m |
| Ink-jet Printing (7) | Gold nanoparticles in toluene | 2-5nm | 30 | 15 μ m |
| Ink-jet Printing (31) | Gold nanoparticles in toluene | 2-4nm | 30 | 20 μ m |
| Ink-jet Printing (32) | Gold nanoparticles in toluene | 5-20nm | 30-50 | 100 μ m |
| Ink-jet Printing (33) | Gold nanoparticles in toluene | 2-4nm | 30 | 125 μ m |
| Ink-jet Printing (34) | Silver nanoparticles in α -terpineol | 5-7nm | 10 | 100 μ m |
| Ink-jet Printing (35) | Silver nanoparticles in toluene | 1-10nm | 30 | 120 μ m |
| Ink-jet Printing (36) | Silver ink in xylene | - | 16 | 160 μ m |
| Ink-jet Printing (37) | Silver nanodispersion | 50nm | 8 | 1.5mm |
| Microcontact Printing (38) | Copper | - | - | 500nm |
| Chemical Vapor Deposition (39) | Copper | - | - | 1 μ m |

**Figure 4**

Micrographs of different tracks produced using the direct write device: (a) the flow rate was set to $5 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and applied voltage was 4.8 kV; and (b) the flow rate was $9.17 \times 10^{-11} \text{ m}^3\text{s}^{-1}$ and applied voltage was 4.1kV. The track width in (b) is $\sim 350\mu\text{m}$

contained the nano-gold particles. A similar kind of particle arrangement has been reported by Cuk et al. (26) in their work with copper particles, and their flow visualization studies identified Bénard–Marangoni convection as the mechanism responsible for formation of multiple lines from a single printed track.

Figure 5 (b) shows a high-resolution SEM image of the edge of the track and Figures 5(c) and (d) shows similar images of the central track where most of the nano-gold particles assemble. From Figure 5(d) it is clear that a considerable proportion of the gold particles are not densely packed, hence leaving voids between particles and obviously this type of particle arrangement is not ideal for producing electrically conducting gold tracks.

The ability to direct write metallic lines $< 20\mu\text{m}$ and having the electrical conductivity of its bulk material would open up a whole new realm of possibilities (1). Table 1 shows the different reported methods used for producing conductive tracks, ink-jet printing is the prime technique, and a minimum track size of about $15\mu\text{m}$ (7) has been achieved after coupling laser technology with ink-jet printing and using a suspension having a gold particle concentration of 300 times than that used in the present work. Experiments using more concentrated metal colloids are underway with the objective of electrohydrodynamic deposition of even finer conductive tracks.

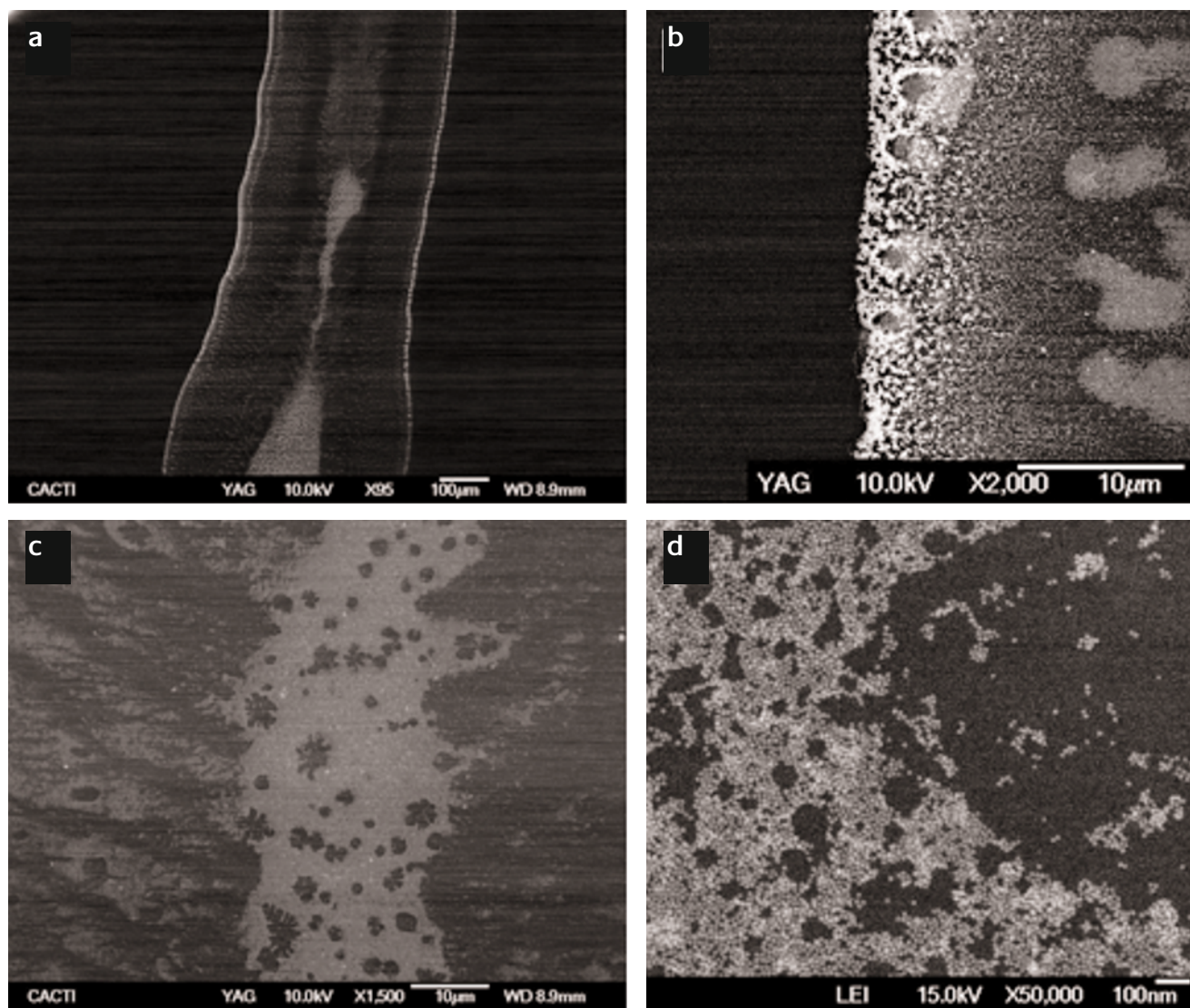


Figure 5

Scanning electron micrographs of the printed track: (a) whole track; (b) an edge track; (c) and (d) centre track

Conclusions

A gold nano-suspension has been subjected to an electrohydrodynamic process and the droplets generated have been deposited using a 2D patterning device in an attempt to directly write metal tracks. Due to the Bénard–Marangoni effect gold particles organize into three lines, having a narrow width compared with the original printed track and do not form continuous gold tracks. We anticipate that the use of a more concentrated suspension may be helpful in this regard, however varying the shape of the gold particles could also improve connectivity and this is also being investigated.

References

- 1 T.W. Ellis, *Gold Bulletin*, 2004, **37**, 66
- 2 J.R. Greenwood, P.R.N. Childs and P. Chaloner, *Gold Bulletin*, 1999, **32**, 85
- 3 G. Humpston, *Gold Bulletin*, 1999, **32**, 75
- 4 G.J. Berry, J.A. Cairns and J. Thomson, *Sensors & Actuators A*, 1995, **51**, 47
- 5 D. Tonneau, J.E. Bouree, A. Correia, G. Roche, G. Pelous and S. Verdeyme, *J. Appl. Phys.*, 1995, **78**, 5139
- 6 H. Sirringhaus and T. Shimoda, *MRS Bulletin*, 2003, **28**, 802
- 7 N.R. Bieri, J. Chung, D. Poulikakos and C.P. Grigoropoulos, *Superlattice Microst.*, 2004, **35**, 437
- 8 H.M. Nur, J.H. Song, J.R.G. Evans and M.J. Edirisinghe, *J. Mater. Sci. – Mater. In Electr.*, 1999, **13**, 213
- 9 S.N. Jayasinghe and M.J. Edirisinghe, *Appl. Phys. A.*, 2005, **80**, 701
- 10 D.Z. Wang, S.N. Jayasinghe and M.J. Edirisinghe, *J. Nanopart. Res.*, 2005, **7**, 301
- 11 A. Jaworek and A. Krupa, *J. Aerosol Sci.*, 1999, **30**, 873
- 12 M. Cloupeau and B. Prunet-foch, *J. Aerosol Sci.*, 1994, **25**, 1143

- 13 S.N. Jayasinghe, R. Dorey, M.J. Edirisinghe and Z. Luklinska, *Appl. Phys. A.*, 2005, **80**, 723
- 14 D.A. Grigoriev, M.J. Edirisinghe and X. Bao, *J.Mater. Res.*, 2002, **17**, 487
- 15 B. Su and K.L. Choy, *Thin Solid Films*, 2002, **361**, 102
- 16 S.N. Jayasinghe and M.J. Edirisinghe, *J. Mater. Sci. Lett.*, 2003, **22**, 1617
- 17 S.N. Jayasinghe, M.J. Edirisinghe and T. De Wilde, *Mater. Res. Innovat.*, 2002, **6**, 92
- 18 S.N. Jayasinghe and M.J. Edirisinghe, *J. Euro. Ceram. Soc.*, 2004, **24**, 2203
- 19 B.V. Enustun and J. Turkevich, *J. Am. Chem. Soc.*, 1693, **85**, 3317
- 20 C. Graf, D.L.J. Vossen, A. Imhof, and A.V. Blaaderen, *Langmuir*, 2003, **19**, 6693
- 21 S.N. Jayasinghe and M.J. Edirisinghe, *J. Appl. Ceram. Tech.*, 2004, **1**, 140
- 22 S.N. Jayasinghe, M.J. Edirisinghe and D.Z. Wang, *Nanotechnology*, 2004, **15**, 1519
- 23 A.M. Ganan-Calvo, J. Davila and S. Barrero, *J. Aerosol Sci.*, 1997, **28**, 249
- 24 D.Z. Wang, S.N. Jayasinghe and M.J. Edirisinghe, *Rev. Sci. Instr.*, 2005, **76**, 075105
- 25 F. Schulz, S. Franzka and G. Schmid, *Adv. Functional Mater.*, 2002, **12**, 532
- 26 T. Cuk, S.M. Troian, C.M. Hong and S. Wagner, *Appl. Phys. Lett.*, 2005, **77**, 2063
- 27 P.M. Mendes, S. Jacke, K. Critchley, J. Plaza, Y. Chen, K. Nikitin, R.E. Palmer, J.A. Preece, S.D. Evans and D. Fitzmaurice, *Langmuir*, 2004, **20**, 3766
- 28 T.Y. Choi, D. Poulikakos and C.P. Grigoropoulos, *Appl. Phys. Lett.*, 2004, **85**, 13
- 29 F. Guan, M.A. Chen, W. Yang, J.Q. Wang, S.R. Yong and Q.J. Xue, *Appl. Surf. Sci.*, 2005, **240**, 24
- 30 S. Corbett, J. Strole and K. Johnston, *Applied Ceramic Technology*, 2005, **2**, 390
- 31 N.R. Bieri, J. Chung, S.E. Haferl, D. Poulikakos and C.P. Grigoropoulos, *Appl. Phys. Lett.*, 2004, **82**, 3529
- 32 J.B. Szczech, C.M. Megaridis, J. Zhang and D.R. Gamota, *Microscale Therm. Eng.*, 2004, **8**, 327
- 33 J. Chung, S. Ko, N.R. Bieri, C.P. Grigoropoulos and D. Poulikakos, *Appl. Phys. Lett.*, 2004, **84**, 801
- 34 S.B. Fuller, E.J. Wilhelm and J.A. Jacobson, *J. Microelectromech. S.*, 2002, **11**, 54
- 35 J.B. Szczech, C.M. Megaridis, D.R. Gamota and J. Zhang, *IEEE Transactions on Electronics Packaging Manufacturing*, 2002, **25**, 26
- 36 A.L. Dearden, P.J. Smith, D.Y. Shin, N. Reis, B. Derby and P. O'Brien, *Macromol. Rapid Comm.*, 2005, **26**, 315
- 37 A. Kamyshny, M. Ben-moshe, S. Aviezer and S. Magdassi, *Macromol Rapid Comm.*, 2004, **26**, 281
- 38 P.C. Hidber, W. Helbig, E. Kim and G.M. Whitesides, *Langmuir*, 1996, **12**, 1375
- 39 S.J. Potochnik, P.E. Pehrsson, D.S.Y. Hsu and J.M. Calvert, *Langmuir*, 1995, **11**, 1841